

NASA TECH BRIEF



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Refractory Oxides Evaluated for High-Temperature Use

The problem: Selecting suitable refractory oxides for use as insulating and heat-storage materials in a high-temperature (3000° to 4000°F) cyclically operated pebble-bed air heater. The consideration of materials for this use was limited to commercial ceramic oxides with melting points above 3000°F.

The solution: A partially calcia-stabilized zirconia is considered to be the best material for the high-temperature zone (3000° to 4000°F) of the heater where high thermal-shock cycles occur. Fully calcia-stabilized zirconia appears to be best for the moderate-temperature zones (1500° to 3000°F) of the pebble bed, the middle sections of the liner, and the insulating brickwork at upper levels. Only very tightly bonded materials such as alumina are considered acceptable for usage in the lower temperature sections of the heater.

How it's done: Pebbles and cubes of the various refractory oxides were subjected to tests for resistance to thermal shock, high-temperature static-load capability, structural breakdown due to crystal instability, and reaction temperatures of dissimilar oxides at interfaces. The materials were heated in an oxyacetylene-fired kiln for the high-temperature tests. Tests for crystal instability were conducted in an electric furnace which was programmed to heat and cool automatically between the desired temperature limits. The results of the tests are summarized below:

1. Fused-grain partially calcia-stabilized zirconia has the best thermal-shock resistance of all the materials tested and is the most acceptable material for

use in the high-temperature sections of heat exchangers for operation above 3400°F.

2. In general, all calcia-stabilized zirconia products exhibited thermal-shock properties superior to the experimental rare-earth (ceria and yttria) stabilized materials available for study.
3. Thoria and magnesia both appear unsuitable for cyclic use at high temperatures because of poor thermal-shock capabilities.
4. Stabilized zirconia undergoes a rapid loss of static load capability above 3000°F; loadings should not exceed approximately 4 to 6 pounds per square inch in high-temperature sections of a zirconia heat exchanger.
5. Deterioration (strength loss) due to crystalline inversion with zirconia products varies with degree of stabilization. In general, fully stabilized products using either calcia or rare-earth materials for stabilization suffer little strength loss on cycling; however, the partially stabilized materials may lose all strength and crumble after as few as 50 cycles in the critical temperature range (approximately 1600° to 2100°F).
6. Indications are that zirconia reacts (forms solid solution on contact) with all other materials tested at temperatures appreciably lower than the normal use temperatures of the individual materials.

Note: Further information concerning this evaluation is given in NASA TN-D-2493, "Evaluation of Selected Refractory Oxide Materials for Use in High-Temperature Pebble-Bed Wind-Tunnel Heat Exchangers", by John D. Buckley and B. W. Cocke, Jr., September 1964, available from the Clearinghouse for

(continued overleaf)

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